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(19)

(11) Publication number:

01

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PATENT ABSTRACTS OF JAPAN

(21) Application number: 07194161

(51) Intl. Cl.: H01M 10/40 H01M 10/36

(22) Application date: 06.07.95

| | | |
|---------------------------------------|----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|
| (30) Priority: | 07.07.94 JP 06179394 | (71) Applicant: RICOH CO LTD |
| (43) Date of application publication: | 22.03.96 | (72) Inventor: OSAWA TOSHIYUKI KAHATA TOSHIYUKI KUROSAWA YOSHIKO KIMURA OKITOSHI FUJII TOSHISHIGE KATAGIRI NOBUO HAYASHI YOSHITAKA |
| (84) Designated contracting states: | | (74) Representative: |

(54) LITHIUM
NONAQUEOUS
SECONDARY BATTERY

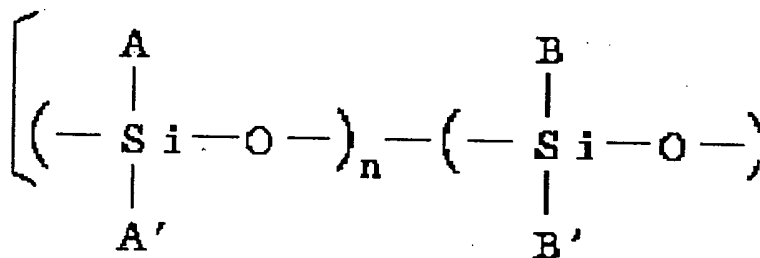
(57) Abstract:

PURPOSE: To obtain a high-performance lithium nonaqueous secondary battery with its excellent cycle characteristics capable of charging even at a high current density by containing a silicone compound is an electrolytic liquid or solid electrolyte.

CONSTITUTION: A compound shown by expression I is contained in electrolytic liquid or solid electrolyte in a nonaqueous secondary lithium battery in which a host compound forming a lithium metal, a lithium alloy, or a lithium ion and an interlayer compound, or complex is formed in a negative pole. In this expression, n stays in a range from 0

to 10, and m and k stay in a range from 1 to 10. A and A' express alkyl groups which may be the same or different from each other, B and B' express an oxyalkylene chain or alkyl group which does not have an active hydrogen which may be the same or different from each other, however, at least one of B and B' is an oxyalkylene chain which does not have any active hydrogen.

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Get Now: [More choices...](#)Tools: Add to Work File: [Create new Wo](#)View: [INPADOC](#) | Jump to: Go to: [Derwent...](#)[Email](#)Title: **JP8078053A2: LITHIUM NONAQUEOUS SECONDARY BATTERY**Country: **JP Japan**Kind: **A**

Inventor: **OSAWA TOSHIYUKI;**
KAHATA TOSHIYUKI;
KUROSAWA YOSHIKO;
KIMURA OKITOSHI;
FUJII TOSHISHIGE;
KATAGIRI NOBUO;
HAYASHI YOSHITAKA;

Assignee: **RICOH CO LTD**
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Published / Filed: **1996-03-22 / 1995-07-06**Application Number: **JP1995000194161**IPC Code: **H01M 10/40; H01M 10/36;**Priority Number: **1994-07-07 JP1994000001793**

Abstract:

PURPOSE: To obtain a high-performance lithium nonaqueous secondary battery with its excellent cycle characteristics capable of charging even at a high current density by containing a silicone compound is an electrolytic liquid or solid electrolyte.

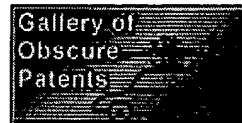
CONSTITUTION: A compound shown by expression I is contained in electrolytic liquid or solid electrolyte in a nonaqueous secondary lithium battery in which a host compound forming a lithium metal, a lithium alloy, or a lithium ion and an interlayer compound, or complex is formed in a negative pole. In this expression, n stays in a range from 0 to 10, and m and k stay in a range from 1 to 10. A and A' express alkyl groups which may be the same or different from each other, B and B' express an oxyalkylene chain or alkyl group which does not have an active hydrogen which may be the same or different from each other, however, at least one of B and B' is an oxyalkylene chain which does not have any active hydrogen.

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Other Abstract Info: **CHEMABS 125(02)015271N CAN125(02)015271N DERABS C96-214260 DERC96-214260**



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(書誌+要約+請求の範囲)

(19)【発行国】日本国特許庁(JP)
(12)【公報種別】公開特許公報(A)
(11)【公開番号】特開平8-78053
(43)【公開日】平成8年(1996)3月22日
(54)【発明の名称】リチウム非水二次電池
(51)【国際特許分類第6版】

H01M 10/40 A
..... 10/36 A

【審査請求】未請求

【請求項の数】6

【出願形態】FD

【全頁数】5

(21)【出願番号】特願平7-194161
(22)【出願日】平成7年(1995)7月6日
(31)【優先権主張番号】特願平6-179394
(32)【優先日】平6(1994)7月7日
(33)【優先権主張国】日本(JP)
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(57)【要約】

【目的】サイクル特性に優れ、かつ高い電流密度でも充電可能な高性能なリチウム非水二次電池の提供。

【構成】正極、リチウム金属、リチウム合金およびリチウムと層間化合物又は錯体を形成するホスト化合物よりなる群から選ばれた少なくとも1種のものを含む負極および電解質を有する非水二次電池において、電解液または固体電解質中にシリコン系化合物を含むことを特徴とするリチウム電池。

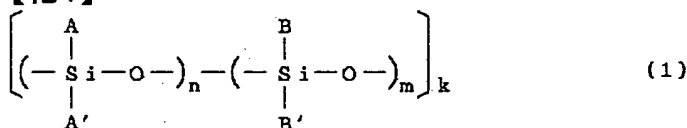
【特許請求の範囲】

【請求項1】正極、リチウム金属、リチウム合金およびリチウムと層間化合物又は錯体を形成するホスト化合物よりなる群から選ばれた少なくとも1種のものを含む負極および電解質を有する非水二次電池において、電解液または固体電解質中にシリコン系化合物を含むことを特徴とするリチウム電池。

【請求項2】請求項1記載のリチウム電池において、シリコン系化合物がSi-O骨格の側鎖にオキシアルキレン鎖が付加した構造のものであるリチウム電池。

【請求項3】請求項1または2記載のリチウム電池において、シリコン系化合物が次式(1)

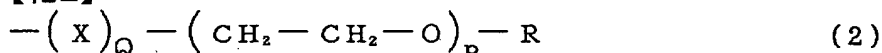
【化1】



(式中、nは0～10、m、kは1～10である。A、A'は、同一または相異なっているよいアルキル基、B、B'は、同一または相異なっているよい活性水素を有しないオキシアルキレン鎖またはアルキル基を表わすが、BおよびB'のうちの少なくとも一方は活性水素を有しないオキシアルキレン鎖である。)で表わされるものであるリチウム電池。

【請求項4】請求項3記載のリチウム電池において、前式(1)で表わされるシリコン系化合物が、BおよびB'のオキシアルキレン鎖が次式(2)

【化2】



(式中、Qは1～5、pは1～10であり、Rは炭素数1～12のアルキル基、Xは炭素数1～6のアルキレン基またはオキシアルキレン鎖を表わす)で表わされるシリコン系化合物。

【請求項5】請求項1、2、3または4記載のリチウム電池において、ホスト化合物の主たる構成成分が、炭素体であるリチウム電池。

【請求項6】請求項1、2、3、4または5記載のリチウム電池において、正極の主たる構成成分が、導電性高分子および／または遷移金属化合物であるリチウム電池。

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平8-78053

(43) 公開日 平成8年(1996)3月22日

| (51) Int. CL. | 識別記号 | 片内登録番号 | P I | 技術表示箇所 |
|---------------|------|--------|-----|--------|
| H 0 1 M 10/40 | A | | | |
| 10/36 | A | | | |

審査請求 未請求 請求項の数 6 F D (全 5 頁)

| | | | |
|--------------|----------------|----------|------------------------------------------|
| (21) 出願番号 | 特願平7-194161 | (71) 出願人 | 000006747 株式会社リコー 東京都大田区中馬込1丁目3番6号 |
| (22) 出願日 | 平成7年(1995)7月6日 | (72) 発明者 | 大塚 利幸 東京都大田区中馬込1丁目3番6号 株式会社リコー内 |
| (31) 優先権主張番号 | 特願平6-179394 | (72) 発明者 | 加藤 利幸 東京都大田区中馬込1丁目3番6号 株式会社リコー内 |
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| (33) 優先権主張国 | 日本 (J P) | (74) 代理人 | 弁理士 友松 英爾 (外1名) 最終頁に続く |

(54) 【発明の名称】 リチウム非水二次電池

(57) 【要約】

【目的】 サイクル特性に優れ、かつ高い電流密度でも充電可能な高性能なリチウム非水二次電池の提供。

【構成】 正極、リチウム金属、リチウム合金およびリチウムと層間化合物又は錯体を形成するホスト化合物よりなる群から選ばれた少なくとも1種のものを含有する負極および電解質を有する非水二次電池において、電解液または固体電解質中にシリコン系化合物を含有することを特徴とするリチウム電池。

(2)

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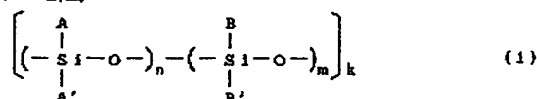
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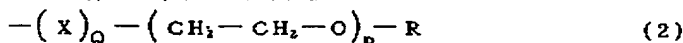
【特許請求の範囲】

【請求項1】 正極、リチウム金属、リチウム合金およびリチウムと層間化合物又は錯体を形成するホスト化合物よりなる群から選ばれた少なくとも1種のものを含有する負極および電解質を有する非水二次電池において、電解質または固体電解質中にシリコン系化合物を含有することを特徴とするリチウム電池。

*



(式中、nは0~10、m、kは1~10である。A、A'は、同一または相異なってもよいアルキル基、B、B'は、同一または相異なってもよい活性水素を有しないオキシアルキレン鎖またはアルキル基を表わすが、BおよびB'のうちの少なくとも一方は活性水素を有しないオキシアルキレン鎖である。)で表わされる※



(式中、Qは1~5、pは1~10であり、Rは炭素数1~12のアルキル基、Xは炭素数1~6のアルキレン基またはオキシアルキレン鎖を表わす)で表わされるシリコン系化合物。

【請求項5】 請求項1、2、3または4記載のリチウム電池において、ホスト化合物の主たる構成成分が、炭素体であるリチウム電池。

【請求項6】 請求項1、2、3、4または5記載のリチウム電池において、正極の主たる構成成分が、導電性高分子および/または遷移金属化合物であるリチウム電池。

【発明の詳細な説明】

【0001】

【技術分野】本発明は、リチウム金属、リチウム合金又はリチウムイオンと層間化合物又は錯体を形成するホスト化合物を負極とする非水二次リチウム電池に関する。

【0002】

【従来技術】リチウム二次電池は理論エネルギー密度が高く、ポータブル電子機器用電源を初め、電気自動車、電力貯蔵用電源としても実用化が期待されている。しかし、金属リチウムを負極に使用したリチウム二次電池は、サイクル寿命、安全性などの点に問題があり、十分な性能のものは開発されていない。この最も大きな理由の一つは負極の性能にあると考えられている。リチウム二次電池の負極の実用上の問題点として、負極である金属リチウムの反応性が高いため、負極表面が溶媒と反応し易い。充電時においてリチウムイオンの還元により生成する金属リチウムはデンドライトとし生成し易く、正、負極間の絶縁層(セパレータ)を破壊するなどの問題である。これらの問題を解決する方法の一つとして電解液の添加剤が検討されている〔森田、青木、松田、電化5

※【請求項2】 請求項1記載のリチウム電池において、シリコン系化合物がSi-O骨格の側鎖にオキシアルキレン鎖が付加した構造のものであるリチウム電池。

【請求項3】 請求項1または2記載のリチウム電池において、シリコン系化合物が次式(1)

【化1】

※ものであるリチウム電池。

【請求項4】 請求項3記載のリチウム電池において、前式(1)で表わされるシリコン系化合物が、BおよびB'のオキシアルキレン鎖が次式(2)

【化2】

7, 523 (1989); M. Morita, S. Aoki and Y. Matsuda, Progress in Batteries & Solar Cells, Vol. 8 (1989)〕。一方、負極材料に、リチウムイオンを自らの層間に取り込んで層間化合物、あるいはリチウム金属として安定化する炭素材料、セラミック材料を使用した負極の開発が進められている。リチウムイオンのインターカレントとしては天然黒鉛、石炭、コークスの他、有機化合物を原料とした熱分解炭素、天然高分子、合成高分子を焼成することにより得られる炭素体があげられる。形態も多孔質粉体から炭素繊維、硝子状炭素等さまざまである。これら負極活性物質用炭素材料としては、例えば、特開平2-66856号公報に負極活性物質として、フルフルリ樹脂を1100℃で焼成した導電性炭素材料を用いることが提案されている。また、特開昭61-277165号公報には、芳香族ポリイミドを不活性雰囲気下で2000℃以上の温度で熱処理して得られる導電性炭素材料を負極活性物質に使用する例が開示され、さらに特開平4-115457号公報には易黒鉛性球状炭素を黒鉛化したものを負極に用いることが提案されている。また特開昭61-77275号公報ではフェノール系高分子を熱処理したポリアセレン構造の絶縁性、あるいは半導体性の炭素材料を電極に用いた二次電池が開示されている。これらのイオン電池系では、サイクル寿命が向上し電池性能は向上するが、一方において電流特性は十分とは言えない。

【0003】

【目的】本発明の目的は、これらのリチウム非水二次電池における電流特性を解決し、サイクル特性に優れ、高い電流密度でも充放電可能な高性能二次リチウム電池を提供することにある。

(3)

特開平8-78053

3

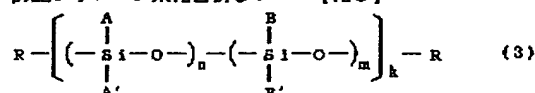
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【0004】

【構成】本発明者らは、前記課題を鋭意検討した結果、リチウム金属、リチウム合金又はリチウムイオンと層間化合物又は錯体を形成するホスト化合物を負極とする非水二次リチウム電池において、シリコン系化合物を電解液または固体電解質中に含有させることにより目的が達せられることを見出した。前記シリコン系化合物と*

※しては、前式(1)で示される化合物が挙げられる。特に、Si-O骨格の側鎖にオキシアルキレンが付加し且つ活性水素の存在が確認されないシリコン系化合物において顕著な効果が見られた。前式(1)で示される化合物をより具体的に示すと、次式(3)で示されるシリコン系化合物が挙げられる。

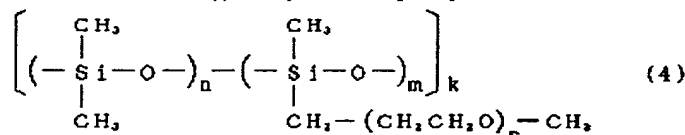
【化3】



前式において、Rは末端基であり、該末端基は同一または相異なったものであってもよく、好ましくはアルキル基。さらに好ましくはメチル基である。A、A'は同一または相異なっているもよい炭素数1~30のアルキル基であり、好ましくは炭素数1~12のアルキル基、さらに好ましくは炭素数1~6のアルキル基である。B、B'はアルキル基または活性水素を有しない同一または相異なっているもよいオキシアルキレン鎖またはアルキル基を表わすが、BおよびB'のうち少なくとも一方は、活性水素を有しないオキシアルキレン鎖である。な※

※お、前記B、B'がオキシアルキレン鎖である場合、好ましくは炭素数1~12のオキシアルキレン鎖。さらに好ましくは炭素数1~6のオキシアルキレン鎖である。また、B、B'がアルキル基である場合、好ましくは炭素数1~12のアルキル基。さらに好ましくは炭素数1~6のアルキル基である。特に下式(4)で示す骨格を有するシリコン系化合物が電流特性を向上せしめ、電池の高エネルギー化にとって有効であることを見出した。

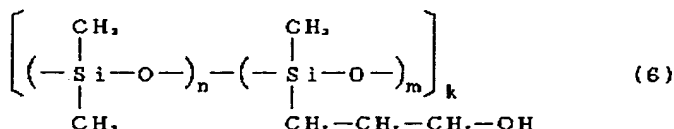
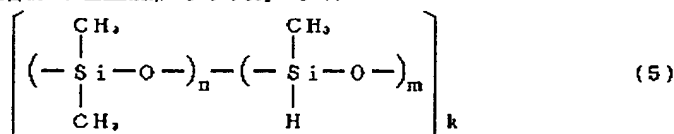
【化4】



シリコン骨格は一般には整泡作用があるため、シリコン化合物は消泡剤として用いられるが、本発明においては、シリコン化合物にアルコキシ基を付加させることにより非水電解液と相溶性を向上せしめたものであり、この結果として非水電池の電極界面の表面エネルギーの低下したためと考えられる。前式(4)の化合物は、下式(5)の化合物に、白金触媒により $CH_2=C$ ★

★ $H-CH_2-OH$ を付加し、下式(6)の化合物とし、さらに該化合物の活性水素をオキシアルキレン鎖で置換することにより得られるが、前式(4)の化合物としては、IRで活性水素を測定し、活性水素が存在しないものが適している。

【化5】



なお、前式(4)、(5)および(6)において、nは0~10、m、r、kは1~10である。前式(1)あるいは(3)の化合物は、固体電解質又は電解液100重量部に対し0.1~30重量部、好ましくは0.1~10重量部用いられる。

【0005】次に本発明の非水二次リチウム電池の構成について具体的に述べるが、基本的には、正極、負極、電解質により構成される。電解液としては非水溶媒に電解質を溶解したものが挙げられる。非水溶媒としては、カーボネート溶媒(プロピレンカーボネート、エチ

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レンカーボネート、ブチレンカーボネート、ジメチルカーボネート、ジエチルカーボネート）、アミド溶媒（N-メチルホルムアミド、N-エチルホルムアミド、N,N-ジメチルホルムアミド、N-メチルアセトアミド、N-エチルアセトアミド、N-メチルピロジリノン）、ラクトン溶媒（γ-ブチラクトン、γ-バレロラクトン、δ-バレロラクトン、3-メチル-1,3-オキサゾリジン-2-オン等）、アルコール溶媒（エチレングリコール、プロピレングリコール、グリセリン、メチルセロソルブ、1,2-ブタンジオール、1,3-ブタンジオール、1,4-ブタンジオール、ジグリセリン、ポリオキシアルキレングリコール、シクロヘキサンジオール、キシレングリコール等）、エーテル溶媒（メチラール、1,2-ジメトキシエタン、1,2-ジエトキシエタン、1-エトキシ-2-メトキシエタン、アルコキシポリアルキレンエーテル等）、ニトリル溶媒（ベンゾニトリル、アセトニトリル、3-メトキシプロピオニトリル等）、燐酸類及び燐酸エステル溶媒（正燐酸、メタ燐酸、ピロ燐酸、ポリ燐酸、亜燐酸、トリメチルホスフェート等）、2-イミダゾリジノン類溶媒（1,3-ジメチル-2-イミダゾリジノン等）、ピロリドン類溶媒、スルホラン溶媒（スルホラン、テトラメチレンスルホラン）、フラン溶媒（テトラヒドロフラン、2-メチルテトラヒドロフラン、2,5-ジメトキシテトラヒドロフラン）、ジオキサラン、ジオキサン、シクロロエタンの単独あるいは2種以上の混合溶媒が使用できる。これらのうち好ましくはカーボネート溶媒、エーテル溶媒、フラン溶媒である。本発明における電解質塩としては、通常の電解質として用いられるものであれば特に制限はないが、例えば、 Li^+BR 、（Rはフェニル基、アルキル基）、 LiPF_6 、 LiSbF_6 、 LiAsF_6 、 LiBF_4 、 LiClO_4 、 $\text{CF}_3\text{SO}_2\text{Li}$ 、 $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ 、 $(\text{CF}_3\text{SO}_2)_2\text{CLi}$ 、 $\text{C}_6\text{F}_5\text{SO}_2\text{Li}$ 、 $\text{C}_6\text{F}_5\text{SO}_2\text{Li}$ 、 LiAlCl_4 、等を例示することができる。好ましくは $\text{CF}_3\text{SO}_2\text{Li}$ 、 $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ 、 $(\text{CF}_3\text{SO}_2)_2\text{CLi}$ 、 $\text{C}_6\text{F}_5\text{SO}_2\text{Li}$ 、 $\text{C}_6\text{F}_5\text{SO}_2\text{Li}$ 等のスルホン酸系アニオンの電解質である。電解液は0.5モル/リットル以上6モル/リットル以内の範囲で調整されるが、好ましくは0.8モル/リットルから3.5モル/リットルの範囲内である。高分子固体電解質としては、ポリエチレンオキサライド、ポリプロピレンオキサライド、ポリフッ化ビニリデン、ポリアクリルアミド等をポリマーマトリクスとし、前記の電解質塩をポリマーマトリクス中に溶解した複合体、あるいはこれらのゲル架橋体、低分子量ポリエチレンオキサライド、クラウンエーテル等のイオン解離基をポリマー主鎖にグラフト化した高分子固体電解質、あるいは、これらにさらに溶媒を加えたゲル、低分子量ポリエチレンオキサライド鎖、クラウンエーテル等のイオン解離基をポリマー骨格中に含む高分子固体電解質、あるいはこれに前

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記電解液を含有させたゲル状高分子固体電解質が挙げられる。

【0006】本発明における負極としてはリチウム金属、アルミニウム、珪素、銅、亜鉛、またはスズなどとリチウムからなるリチウム合金、リチウムイオンを可逆に吸蔵、放出可能な宿主化合物である炭素材料、セラミック材料が例示できる。炭素材料としては、天然高分子あるいはフェノール系樹脂、PAN系樹脂、フラン系樹脂、ポリアミド系樹脂、ポリアミド系樹脂などの合成高分子を焼成することにより得られる導電性炭素体あるいは絶縁性または半導電性の炭素体が例示できる。本発明の炭素体としては主たる構成成分として黒鉛材料を用いることが好ましい。本発明の黒鉛材料としては、天然黒鉛の他、ピッチコークス、ニードルコークス、フリューードコークス、ギルソナコークス等を原料とした人造黒鉛が例示できる。本発明の非水二次リチウム電池の正極活物質としては、 MnO_2 、 Mn_2O_3 、 CoO_2 、 NiO 、 TiO_2 、 V_2O_5 、 V_6O_{13} 、 Cr_2O_3 、 $\text{Fe}_2(\text{SO}_4)_3$ 、 $\text{Fe}_2(\text{MoO}_4)_3$ 、 $\text{Fe}_2(\text{WO}_4)_3$ 等の金属酸化物、 TiS_2 、 MoS_2 、 FeS 等の金属硫化物、これらの化合物とリチウムの複合酸化物、ポリアセチレン、ポリアニリン、ポリピロール、ポリチオフェン、ポリアルキルチオフェン、ポリカルバゾール、ポリアズレン、ポリジフェニルベンジジン等の導電性高分子、炭素体から選ばれる1種またはそれ以上の複合体等を例示することができる。電解質としては、前述した電解液、固体電解質が用いられる。また必要によりセパレータが使用できる。セパレータとしては、電解質溶液のイオン移動に対して低抵抗であり、かつ、溶液保持性に優れたものが用いられ、例えば、ガラス、ポリエステル、テフロン、ポリプロピレン等の1種以上の材質から選ばれる不織布又は織布が挙げられる。本発明の電池の形態は特に限定するものではないが、コイン、シート、円筒、ガム等種々の形態の電池に実装することができる。以下実施例により本発明をさらに具体的に説明する。

【0007】


【実施例】

実施例1

ポリアニリン30重量部を170重量部のN-メチル-2-ピロリドンに溶解し、さらに五酸化バナジウム70重量部をサンドミルで分散した。本塗料溶液を25μmのエッチドアルミ箔の両面にブレードコーターで塗布乾燥し、片面60μmの正極とした。純度99.9%の天然黒鉛80重量部、テトラフルオロホウ酸リチウム10重量部をポリビニルピリジン系樹脂（広栄化学）の10wt%N-メチル-2-ピロリドン溶液100重量部に分散し負極塗料溶液としSUS箔（20μmの厚み）の両面に片面の厚みが80μmになるように負極活物質層を作成した（乾燥温度100℃）。正極と負極を、25μmのセパレータ【セルガード3501、商品名（ダイ

JP,08-078053,A

☒ STANDARD ☐ ZOOM-UP ROTATION

No Rotation 

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セル社製)] を介して積層し、捲回してAAサイズの電池とした。電解液として $(CF_3SO_2)_2NLi$ を2モル/リットル含有したエチレンカーボネート/ジメトキシエタン (1:1) 溶媒に、前記 (3) 式において、 n 、 m が1、および r と k が3の両末端がメチル基であるシリコン系化合物を前記溶液に対し3重量%添加し使用した。比較はシリコン系化合物を除いたものを比較例1として行なった。本実施例および比較例1の電池の電池特性を表1に示した。

【0008】実施例2

電解液の替わりに以下に示す固体電解質溶液を用いた以外は実施例1と同様とした。テトラフルオロホウ酸リチウム

*ウム20重量部、プロピレンカーボネート51重量部、1,2-ジメトキシエタン16重量部、ポリオキシエチレンアクリレート12.8重量部、トリメチロールプロパンアクリレート0.2重量部、ベンゾインイソプロピルエーテル0.02重量部よりなる光重合性溶液を高分子固体電解質溶液とした。該固体電解質溶液に、実施例1で使用したシリコン系化合物を同量添加した。本調整液は電解液と同様注液した後、加熱して固体化する。比較はシリコン系化合物を除いたものを比較例2として行なった。本実施例及び比較例2の電池特性を表1に示した。

【表1】

| | 実施例1 | 実施例2 | 比較例1 | 比較例2 |
|-----------|--------|--------|--------|--------|
| エネルギー | 485mAh | 465mAh | 388mAh | 370mAh |
| サイクル特性 | 500回 | 500回 | 350回 | 400回 |
| 2CmA放電 | 88% | 81% | 66% | 58% |
| 1CmA1時間充電 | 86% | 80% | 74% | 69% |

エネルギー : 1/2CmAで充放電を10回繰り返した後の放電エネルギー

サイクル特性 : 1/2CmAの充放電でエネルギーが70%になるまでのサイクル回数。

2CmA放電、1CmA1時間充電 : 上記エネルギーに対する発現率

2CmA放電 : 2CmA定電流2.5Vカットオフ放電※

※1CmA1時間充電 : 1CmA定電流3.7V低電圧充電1時間

【0009】

【効果】本発明によると、サイクル特性に優れ、かつ高い電流密度でも充電可能な高性能な非水リチウム二次電池が提供された。

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セル社製)を介して積層し、捲回してAAサイズの電池とした。電解液として(CF₃SO₂)₂NLiを2モル/リットル含有したエチレンカーボネート/ジメトキシエタン(1:1)溶媒に、前記(3)式において、n、mが1、およびrとkが3の両末端がメチル基であるシリコン系化合物を前記溶液に対し3重量%添加し使用した。比較はシリコン系化合物を除いたものを比較例1として行なった。本実施例および比較例1の電池の電池特性を下表1に示した。

【0008】実施例2

電解液の替わりに以下に示す固体電解質溶液を用いた以外は実施例1と同様とした。テトラフルオロホウ酸リチウム

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*ウム20重量部、プロピレンカーボネート51重量部、1,2-ジメトキシエタン16重量部、ポリオキシエチレンアクリレート12.8重量部、トリメチロールプロパンアクリレート0.2重量部、ベンゾインイソプロピルエーテル0.02重量部よりなる光重合性溶液を高分子固体電解質溶液とした。該固体電解質溶液に、実施例1で使用したシリコン系化合物を同量添加した。本調整液は電解液と同様注液した後、加熱して固体化する。比較はシリコン系化合物を除いたものを比較例2として行なった。本実施例及び比較例2の電池特性を下表1に示した。

【表1】

| | 実施例1 | 実施例2 | 比較例1 | 比較例2 |
|-----------|--------|--------|--------|--------|
| エネルギー | 485mAh | 465mAh | 388mAh | 370mAh |
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2CmA放電、1CmA1時間充電：上記エネルギーに対する発現率

2CmA放電：2CmA定電流2.5Vカットオフ放電※

※1CmA1時間充電：1CmA定電流3.7V低電圧充電1時間

【0009】

【効果】本発明によると、サイクル特性に優れ、かつ高い電流密度でも充電可能な高性能な非水リチウム二次電池が提供された。

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特開平8-78053

【公報種別】特許法第17条の2の規定による補正の掲載
 【部門区分】第7部門第1区分
 【発行日】平成11年(1999)12月14日

【公開番号】特開平8-78053
 【公開日】平成8年(1996)3月22日
 【年通号数】公開特許公報8-781
 【出願番号】特願平7-194161
 【国際特許分類第6版】

H01M 10/40

10/36

【F1】

H01M 10/40

A

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【手続補正言】

【提出日】平成11年3月26日

【手続補正1】

【補正対象音類名】明細書

【補正対象項目名】請求項1

【補正方法】変更

【補正内容】

【請求項1】正極およびリチウム金属、リチウム合金、リチウムと層間化合物又は錯体を形成するホスト化合物よりなる群から選ばれた少なくとも1種の活物質を含有する負極および電解質を有する非水二次電池において、電解質または固体電解質中にシリコン系化合物を含有することを特徴とするリチウム電池。

【手続補正2】

【補正対象音類名】明細書

【補正対象項目名】0001

【補正方法】変更

【補正内容】

【0001】

【技術分野】本発明は、リチウム金属、リチウム合金又はリチウムイオンと層間化合物又は錯体を形成するホスト化合物を活性物質とする負極を有する非水二次リチウム*

*電池に関する。

【手続補正3】

【補正対象音類名】明細書

【補正対象項目名】0004

【補正方法】変更

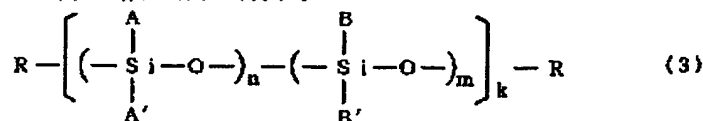
【補正内容】

【0004】

【構成】本発明者らは、前記課題を鋭意検討した結果、リチウム金属、リチウム合金又はリチウムイオンと層間化合物又は錯体を形成するホスト化合物を活性物質とする負極を有する非水二次リチウム電池において、シリコン系化合物を電解質または固体電解質中に含有させることにより目的が達せられることを見出した。前記シリコン系化合物としては、前式(1)で示される化合物が挙げられる。特に、Si-O骨格の側鎖にオキシアルキレンが付加し且つ活性水素の存在が確認されないシリコン系化合物において顕著な効果が見られた。前式

(1)で示される化合物をより具体的に示すと、次式(3)で示されるシリコン系化合物が挙げられる。

【化3】



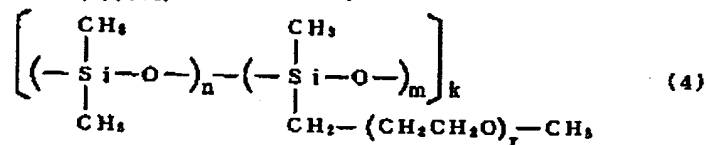
前式において、Rは末端基であり、該末端基は同一または相異なったものであってもよく、好ましくはアルキル基、さらに好ましくはメチル基である。A、A'は同一または相異なっているいてもよい炭素数1~30のアルキル基であり、好ましくは炭素数1~12のアルキル基、さらに好ましくは炭素数1~6のアルキル基である。B、B'は活性水素を有しない同一または相異なっているいてもよいオキシアルキレン鎖またはアルキル基を表わすが、

BおよびB'のうち少なくとも一方は、活性水素を有しないオキシアルキレン鎖である。なお、前記B、B'がオキシアルキレン鎖である場合、好ましくは炭素数1~12のオキシアルキレン鎖、さらに好ましくは炭素数1~6のオキシアルキレン鎖である。また、B、B'がアルキル基である場合、好ましくは炭素数1~12のアルキル基、さらに好ましくは炭素数1~6のアルキル基である。特に下式(4)で示す骨格を有するシリコン系

-補1-

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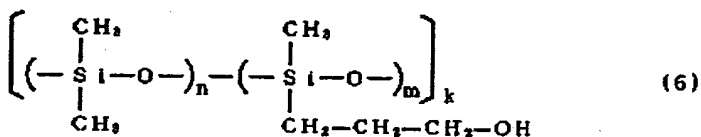
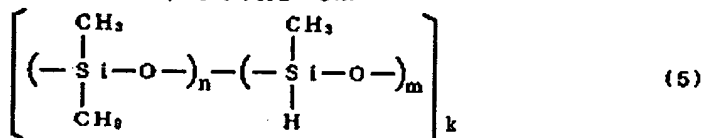
化合物が電流特性を向上せしめ、電池の高エネルギー化 * 【化4】
 にとって有効であることを見出した。 *



シリコン骨格は一般には整泡作用があるため、シリコン化合物は消泡剤として用いられるが、本発明においては、シリコン化合物にアルコキシ基を付加させることにより非水電解液と相溶性を向上せしめたものであり、この結果として非水電池の電極界面の表面エネルギーの低下したためと考えられる。前式(4)の化合物は、下式(5)の化合物に、白金触媒により $\text{CH}_2=\text{C}^*$

* $\text{H}-\text{CH}_2-\text{OH}$ を付加し、下式(6)の化合物とし、さらに該化合物の活性水素をオキシアルキレン鎖で置換することにより得られるが、前式(4)の化合物としては、IRで活性水素を測定し、活性水素が存在しないものが適している。

【化5】



なお、前式(4)、(5)および(6)において、 n は0~10、 m 、 r 、 k は1~10である。前式(1)あるいは(3)の化合物は、固体電解質又は電解液100

重量部に対し0.1~30重量部、好ましくは0.1~10重量部用いられる。

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CLAIMS

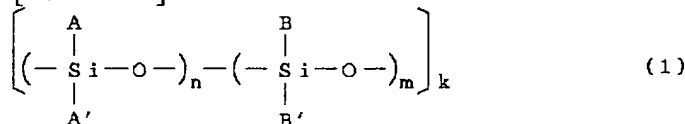
[Claim(s)]

[Claim 1] The lithium cell characterized by containing a silicone system compound in the electrolytic solution or a solid electrolyte in the non-water rechargeable battery which has the negative electrode and electrolyte containing at least one sort of things chosen from the group which consists of a host compound which forms a positive electrode, a lithium metal, a lithium alloy and a lithium, an intercalation compound, or a complex.

[Claim 2] The lithium cell which is the thing of the structure which the oxy-alkylene chain added [the silicone system compound] to the side chain of an Si-O skeleton in the lithium cell according to claim 1.

[Claim 3] It sets to a lithium cell according to claim 1 or 2, and a silicone system compound is the following formula (1).

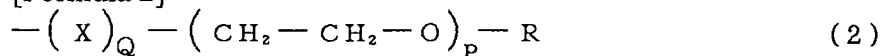
[Formula 1]



(0-10, and m and k of n are 1-10 among a formula.) Same or alkyl group [which may be different from each other], B, and B' of A and A' is the same or an oxy-alkylene chain with which at least one side of B and B' does not have active hydrogen although the oxy-alkylene chain or alkyl group which does not have active hydrogen which may be different from each other is expressed. Lithium cell which is what is expressed.

[Claim 4] For the silicone system compound expressed with a front formula (1) in a lithium cell according to claim 3, the oxy-alkylene chain of B and B' is the following formula (2).

[Formula 2]



It is the silicone system compound expressed with (1-5p of Q are 1-10 among a formula, R expresses the alkyl group of carbon numbers 1-12, and X expresses the alkylene machine or oxy-alkylene chain of carbon numbers 1-6).

[Claim 5] The lithium cell whose main constituent of a host compound is a carbon body in a lithium cell according to claim 1, 2, 3, or 4.

[Claim 6] The lithium cell whose main constituents of a positive electrode are a conductive polymer and/or a transition-metals compound in a lithium cell according to claim 1, 2, 3, 4, or 5.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention relates to the non-water secondary lithium cell which uses as a negative electrode the host compound which forms a lithium metal, a lithium alloy or a lithium ion, an intercalation compound, or a complex.

[0002]

[Description of the Prior Art] The theoretical energy density of a lithium secondary battery is high, and the power supply for portable electronic equipment is expected to utilization also as an electric vehicle and a power supply for power storage at first. However, second lithium ** which used the metal lithium for the negative electrode has a problem in points, such as a cycle life and safety, and the thing of sufficient performance is not developed. It is thought that one of the biggest reason of this is in the performance of a negative electrode. Since the reactivity of the metal lithium which is a negative electrode is high as a trouble that the negative electrode of a lithium secondary battery is practical, a negative-electrode front face tends to react with a solvent. The metal lithium generated by reduction of a lithium ion at the time of charge is the problem of considering as a dendrite, being easy to generate and destroying the insulating layer between positive and a negative electrode (separator). The additive of the electrolytic solution is examined as one of the methods of solving these problems [Morita, Aoki, Matsuda, electrification 57,523(1989);M.Morita, S.Aoki and Y.Matsuda, Progress in Batteries & Solar Cells, Vol.8 (1989)]. Development of the negative electrode which used the carbon material which incorporates a lithium ion between its layers into negative-electrode material, and is stabilized as an intercalation compound or a lithium metal into it on the other hand, and ceramic material is furthered. The carbon body obtained by calcinating the pyrolytic carbon which used the organic compound besides a natural graphite, coal, and corks as the raw material as interchange car RANTO of a lithium ion, naturally-occurring polymers, and a synthetic macromolecule is raised. The gestalt of a carbon fiber and glass-like carbon is also various from porosity fine particles. Using for JP,2-66856,A the conductive carbon material which calcinated the furfuryl resin at 1100 degrees C, for example as a negative-electrode active material as a carbon material for these negative-electrodes active materials is proposed. Moreover, the example which uses the conductive carbon material which heat-treats an aromatic polyimide at the temperature of 2000 degrees C or more under an inert atmosphere, and is obtained for a negative-electrode active material is indicated by JP,61-277165,A, and using for a negative electrode what graphitized ***** spherical carbon is further proposed by JP,4-115457,A at it. Moreover, in JP,61-77275,A, the rechargeable battery which used for the electrode the carbon material of the insulation of the poly acene structure which heat-treated the phenol system macromolecule, or semiconductor nature is indicated. Although a cycle life improves and a cell performance improves in these ion fuel cell subsystems, in one side, it cannot be said that a current characteristic is enough.

[0003]

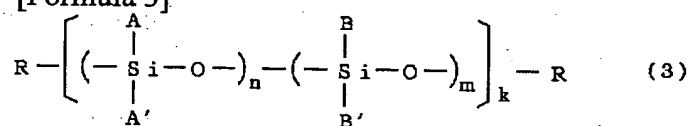
[Objects of the Invention] The purpose of this invention solves the current characteristic in these

lithium non-water rechargeable batteries, is excellent in a cycle property, and is to offer the highly efficient secondary lithium cell in which charge and discharge are possible also with high current density.

[0004]

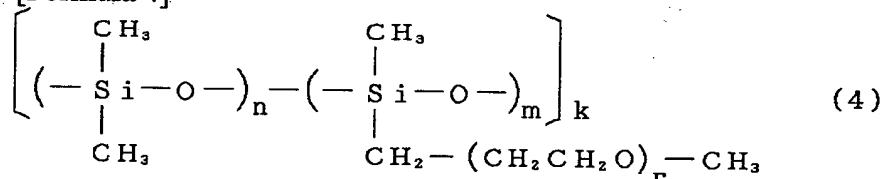
[Elements of the Invention] This invention persons found out that the purpose was reached in the non-water secondary lithium cell which uses as a negative electrode the host compound which forms a lithium metal, a lithium alloy or a lithium ion, an intercalation compound, or a complex by making a silicone system compound contain in the electrolytic solution or a solid electrolyte, as a result of examining the aforementioned technical problem wholeheartedly. As the aforementioned silicone system compound, the compound shown by the front formula (1) is mentioned. The remarkable effect was seen in the silicone system compound with which an oxy-alkylene adds to the side chain of an Si-O skeleton, and existence of active hydrogen is not checked especially. If the compound shown by the front formula (1) is shown more concretely, the silicone system compound shown by the following formula (3) will be mentioned.

[Formula 3]



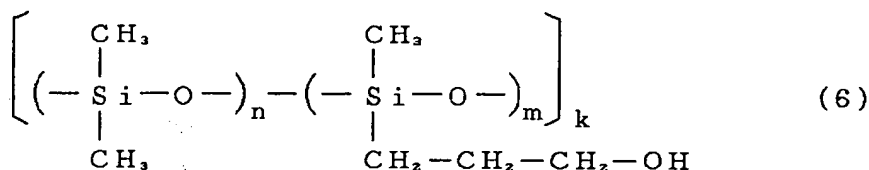
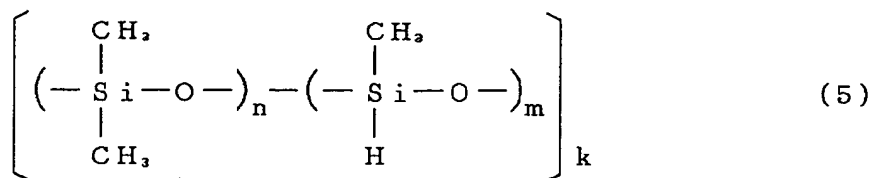
in a front formula, R is an end group and this end group is the same -- or -- being different from each other -- desirable -- an alkyl group -- it is a methyl group still more preferably A and A' is the same or the alkyl group of carbon numbers 1-30 which may be different from each other, and is the alkyl group of carbon numbers 1-6 preferably [it is desirable and] to the alkyl group of carbon numbers 1-12, and a pan. B and B' is an oxy-alkylene chain which does not have an alkyl group or active hydrogen and with which at least one side does not have active hydrogen among B and B', although the same, the oxy-alkylene chain which may be different from each other, or an alkyl group is expressed. In addition, when Above B and B' are oxy-alkylene chains, it is the oxy-alkylene chain of carbon numbers 1-6 preferably [it is desirable and] to the oxy-alkylene chain of carbon numbers 1-12, and a pan. Moreover, when B and B' is an alkyl group, it is the alkyl group of carbon numbers 1-6 preferably [it is desirable and] to the alkyl group of carbon numbers 1-12, and a pan. The silicone system compound which has the skeleton shown especially by the lower formula (4) made the current characteristic improve, and found out that it was effective for high-energy-izing of a cell.

[Formula 4]



Since a silicone skeleton generally has a ready bubble operation, although a silicon compound is used as a defoaming agent, in this invention, by making an alkoxy group add to a silicon compound, nonaqueous electrolyte and compatibility are made to improve and it thinks because the surface energy of the electrode interface of a non-water battery fell as this result. Although the compound of a front formula (4) is obtained by adding $CH_2=CH-CH_2-OH$ by the platinum catalyst, considering as the compound of a lower formula (6), and replacing the active hydrogen of this compound by the compound of a lower formula (5) with an oxy-alkylene chain further, as a compound of a front formula (4), active hydrogen is measured by IR and that in which active hydrogen does not exist is suitable.

[Formula 5]



In addition, in a front formula (4), (5), and (6), 0-10, and m, r and k of n are 1-10. a front formula (1) or the compound of (3) -- a solid electrolyte or the electrolytic-solution 100 weight section -- receiving -- 0.1 - 30 weight section -- desirable -- 0.1 - 10 weight *****

[0005] Next, although the composition of the non-water secondary lithium cell of this invention is described concretely, fundamentally, it is constituted by a positive electrode, a negative electrode, and the electrolyte. What dissolved the electrolyte salt in the non-aqueous solvent as the electrolytic solution is mentioned. as a non-aqueous solvent -- a carbonate solvent (propylene carbonate and ethylene carbonate --) Butylene carbonate, dimethyl carbonate, diethyl carbonate, an amide solvent (N-methyl formamide, N-ethyl formamide, and N.N-dimethylformamide --) N-methyl acetamide, N-ethyl acetamide, N-methyl PIROJIRINON, a lactone solvent (gamma-butyl lactone, gamma-valerolactone, and delta-valerolactone --) alcoholic solvents (ethylene glycol --), such as the 3-methyl-1 and 3-oxazolidine-2-ON A propylene glycol, a glycerol, a methyl cellosolve, 1, 2-butanediol, 1, 3-butanediol, 1, 4-butanediol, a diglycerol, Polyoxy alkylene glycol, a cyclohexane diol, a xylene glycol, etc., an ether solvent (a methylal, 1, 2-dimethoxyethane, 1, and 2-diethoxy ethane --) 1-ethoxy-2-methoxyethane, the alkoxy polyalkylene ether, etc., A nitril solvent (a benzonitrile, an acetonitrile, 3-methoxy propionitrile, etc.), phosphoric acid and a phosphoric-ester solvent (an orthophosphoric acid, a metaphosphoric acid, a pyrophosphoric acid, and a polyphosphoric acid --) 2-imidazolidinone solvents (1, 3-dimethyl-2-imidazolidinone, etc.), such as a phosphorous acid and trimethyl phosphate, A pyrrolidones solvent, a sulfolane solvent (a sulfolane, tetramethylen sulfolane), A furan solvent (a tetrahydrofuran, 2-methyl tetrahydrofuran, 2, 5-dimethoxy tetrahydrofuran), a dioxolane, a dioxane, and independent or two or more sorts of mixed solvents of a dichloroethane can be used. They are a carbonate solvent, an ether solvent, and a furan solvent preferably [among these]. Although there will be especially no limit if used as a usual electrolyte as an electrolyte salt in this invention For example, LiBR₄ (R is a phenyl group and an alkyl group), LiPF₆, LiSbF₆, LiAsF₆, LiBF₄, LiClO₄, CF₃SO₃Li, (CF₃SO₂)₃NLi, 3(CF₃SO₂) CLi, C₆F₉SO₃Li, and C₈F₁₇SO₃ -- Li, LiAlCl₄, etc. can be illustrated It is the electrolyte of sulfonic-acid system anions, such as CF₃SO₃Li, 3(CF₃SO₂) NLi, 3(CF₃SO₂) CLi, C₆F₉SO₃Li, and C₈F₁₇SO₃Li, preferably. Although the electrolytic solution is adjusted in the 0.5 mols/l. or more less than six mols [/l.] range, it is within the limits of 3.5 mols/l. from 0.8 mols/l. preferably. As a solid polymer electrolyte, a polyethylene oxide, polypropylene oxide, A polyvinylidene fluoride, a polyacrylamide, etc. are made into a polymer matrix. The complex which dissolved the aforementioned electrolyte salt into the polymer matrix, or these gel bridge formation objects, The solid polymer electrolyte which graft-ized ionic dissociation machines, such as a low-molecular-weight polyethylene oxide and a crown ether, to the polymer principal chain, Or the solid polymer electrolyte which contains ionic dissociation machines, such as gel which added the solvent to these further, a low-molecular-weight polyethylene-oxide chain, and a crown ether, in a polymer skeleton, or the gel solid polymer electrolyte which made this contain the aforementioned electrolytic solution is mentioned.

[0006] The lithium alloy which consists of a lithium metal, aluminum, silicon, copper, zinc or tin,

and a lithium as a negative electrode in this invention, the carbon material which are occlusion and the host compound which can be emitted irreversibly about a lithium ion, and ceramic material can be illustrated. The conductive carbon body or the insulating or half-conductive carbon body obtained as a carbon material by calcinating synthetic macromolecules, such as naturally-occurring polymers or a phenol system resin, a PAN system resin, a furan system resin, a polyamide system resin, and a polyimide system resin, can be illustrated. It is desirable to use graphite material as a main constituent as a carbon body of this invention. As a graphite material of this invention, the artificial graphite which used pitch coke besides a natural graphite, a needle coke, a fluid coke, gill box sonar corks, etc. as the raw material can be illustrated. As a positive active material of the non-water secondary lithium cell of this invention MnO_2 , Mn_2O_3 , CoO_2 , NiO_2 and TiO_2 , V_2O_5 , V_3O_8 , Cr_2O_3 , $\text{Fe}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{MoO}_4)_3$, the metallic oxide of $\text{Fe}_2(\text{WO}_4)_3$ grade, Metallic sulfide, such as TiS_2 , MoS_2 , and FeS , these compounds, and the multiple oxide of a lithium, One sort or complex beyond it chosen from conductive polymers, such as a polyacetylene, the poly aniline, polypyrrole, the poly thiophene, the poly alkyl thiophene, the poly carbazole, the poly azulene, and a poly diphenyl benzidine, and a carbon body can be illustrated. As an electrolyte, the electrolytic solution mentioned above and a solid electrolyte are used. Moreover, separator can be used as occasion demands. The nonwoven fabric or textile fabrics which is low resistance, and the thing excellent in solution retentivity is used, for example, is chosen from one or more sorts of quality of the materials, such as glass, polyester, Teflon, and polypropylene, to the ionic migration of an electrolytic solution as separator is mentioned. Although especially the gestalt of the cell of this invention is not limited, it can mount in the cell of various gestalten, such as coin, a sheet, a cylinder, and gum. An example explains this invention still more concretely below.

[0007]

[Example]

The example 1 poly aniline 30 weight section was dissolved in the N-methyl-2-pyrrolidone of the 170 weight sections, and the vanadium-pentoxide 70 weight section was further distributed by the sand mill. Application dryness was carried out by the blade coating machine, and this paint solution was made into the positive electrode of 60 micrometers of one side at both sides of 25-micrometer etched aluminum foil. The negative-electrode active material layer was created so that the natural-graphite 80 weight section of 99.9% of purity and the tetrapod fluoroboric-acid lithium 10 weight section might be distributed in the 10wt% N-methyl-2-pyrrolidone solution 100 weight section of a polyvinyl-pyridine system resin (extensive glory chemistry), it might consider as a negative-electrode paint solution and the thickness of one side might be set to 80 micrometers at both sides of an SUS foil (thickness of 20 micrometers) (drying temperature of 100 degrees C). Through 25-micrometer separator [Celgard 3501 and a tradename (die cell company make)], the laminating of a positive electrode and the negative electrode was carried out, they were wound, and it considered as the cell of AA size. In the aforementioned (3) formula, to the aforementioned solution, m added to the ethylene carbonate / dimethoxyethane (1:1) solvent which contained two mol /of 2NLi(s) l. as the electrolytic solution (CF_3SO_2) 3% of the weight, and used for it the silicone system compound which the both ends of 1, and r and k3 are n, and is a methyl group. Comparison performed the thing except the silicone system compound as an example 1 of comparison. The cell property of the cell of this example and the example 1 of comparison was shown in the following table 1.

[0008] It was presupposed that it is the same as that of an example 1 except having used the solid electrolyte solution shown below instead of the example 2 electrolytic solution. The photopolymerization nature solution which consists of the tetrapod fluoroboric-acid lithium 20 weight section, the propylene carbonate 51 weight section, 1, the 2-dimethoxyethane 16 weight section, the polyoxyethylene acrylate 12.8 weight section, the trimethylol-propane acrylate 0.2 weight section, and the benzoin-iso-propyl-ether 0.02 weight section was used as the solid-polymer-electrolyte solution. The amount addition of said of the silicone system compound used for this solid electrolyte solution in the example 1 was carried out. This adjustment liquid is heated and solidified

after pouring in like the electrolytic solution. Comparison performed the thing except the silicone system compound as an example 2 of comparison. The cell property of this example and the example 2 of comparison was shown in the following table 1.

[Table 1]

example 1 66% 58% 1CmA 1 hour charge 86% 80% 74% 69% Energy : It is charge and discharge at 1/2CmA. Example 2 Example 1 of comparison Example of comparison 2 energy 485mAh 465mAh 388mAh 370mAh cycle property 500 times 500 times 350 times 400 times CmA [2] electric discharge 88% 81% The spark-discharge-energy cycle property after repeating 10 times: The number of times of a cycle until energy becomes 70% by the charge and discharge of 1/2CmA.

2CmA electric discharge, 1CmA 1 hour charge: Incidence-rate 2CmA electric discharge: 2CmA constant-current 2.5V cut-off electric discharge 1CmA 1 hour charge: 1CmA constant-current 3.7V low-battery charge 1 hour to the above-mentioned energy. [0009]

[Effect] According to this invention, the highly efficient non-water lithium secondary battery which is excellent in a cycle property and can be charged also with high current density was offered.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] this invention relates to the non-water secondary lithium cell which uses as a negative electrode the host compound which forms a lithium metal, a lithium alloy or a lithium ion, an intercalation compound, or a complex.

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PRIOR ART

[Description of the Prior Art] The theoretical energy density of a lithium secondary battery is high, and the power supply for portable electronic equipment is expected to utilization also as an electric vehicle and a power supply for power storage at first. However, second lithium ** which used the metal lithium for the negative electrode has a problem in points, such as a cycle life and safety, and the thing of sufficient performance is not developed. It is thought that one of the biggest reason of this is in the performance of a negative electrode. Since the reactivity of the metal lithium which is a negative electrode is high as a trouble that the negative electrode of a lithium secondary battery is practical, a negative-electrode front face tends to react with a solvent. The metal lithium generated by reduction of a lithium ion at the time of charge is the problem of considering as a dendrite, being easy to generate and destroying the insulating layer between positive and a negative electrode (separator). The additive of the electrolytic solution is examined as one of the methods of solving these problems [Morita, Aoki, Matsuda, electrification 57,523(1989); M. Morita, S. Aoki and Y. Matsuda, Progress in Batteries & Solar Cells, Vol.8 (1989)]. Development of the negative electrode which used the carbon material which incorporates a lithium ion between its layers into negative-electrode material, and is stabilized as an intercalation compound or a lithium metal into it on the other hand, and ceramic material is furthered. The carbon body obtained by calcinating the pyrolytic carbon which used the organic compound besides a natural graphite, coal, and corks as the raw material as interchange car RANTO of a lithium ion, naturally-occurring polymers, and a synthetic macromolecule is raised. The gestalt of a carbon fiber and glass-like carbon is also various from porosity fine particles. Using for JP,2-66856,A the conductive carbon material which calcinated the furfuryl resin at 1100 degrees C, for example as a negative-electrode active material as a carbon material for these negative-electrodes active materials is proposed. Moreover, the example which uses the conductive carbon material which heat-treats an aromatic polyimide at the temperature of 2000 degrees C or more under an inert atmosphere, and is obtained for a negative-electrode active material is indicated by JP,61-277165,A, and using for a negative electrode what graphitized ***** spherical carbon is further proposed by JP,4-115457,A at it. Moreover, in JP,61-77275,A, the rechargeable battery which used for the electrode the carbon material of the insulation of the poly acene structure which heat-treated the phenol system macromolecule, or semiconductor nature is indicated. Although a cycle life improves and a cell performance improves in these ion fuel cell subsystems, in one side, it cannot be said that a current characteristic is enough.

[0003]

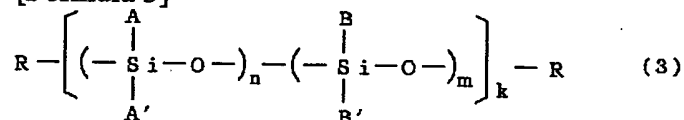
[Objects of the Invention] The purpose of this invention solves the current characteristic in these lithium non-water rechargeable batteries, is excellent in a cycle property, and is to offer the highly efficient secondary lithium cell in which charge and discharge are possible also with high current density.

[0004]

[Elements of the Invention] This invention persons found out that the purpose was reached in the non-water secondary lithium cell which uses as a negative electrode the host compound which forms a lithium metal, a lithium alloy or a lithium ion, an intercalation compound, or a complex by making a silicone system compound contain in the electrolytic solution or a solid electrolyte, as a result of examining the aforementioned technical problem wholeheartedly. As the aforementioned silicone system compound, the compound shown by the front formula (1) is mentioned. The remarkable effect

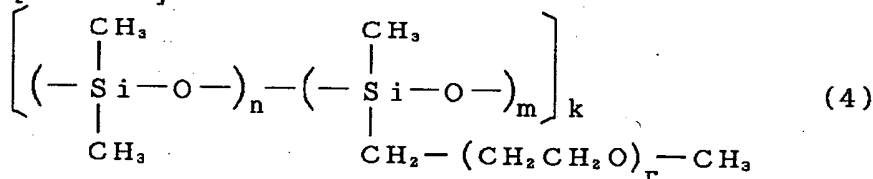
was seen in the silicone system compound with which an oxy-alkylene adds to the side chain of an Si-O skeleton, and existence of active hydrogen is not checked especially. If the compound shown by the front formula (1) is shown more concretely, the silicone system compound shown by the following formula (3) will be mentioned.

[Formula 3]



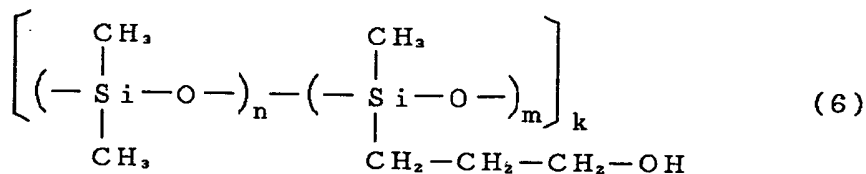
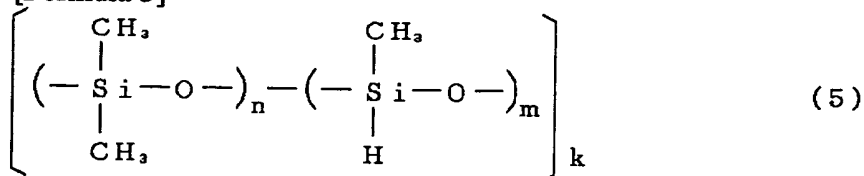
in a front formula, R is an end group and this end group is the same -- or -- being different from each other -- desirable -- an alkyl group -- it is a methyl group still more preferably A and A' is the same or the alkyl group of carbon numbers 1-30 which may be different from each other, and is the alkyl group of carbon numbers 1-6 preferably [it is desirable and] to the alkyl group of carbon numbers 1-12, and a pan. B and B' is an oxy-alkylene chain which does not have an alkyl group or active hydrogen and with which at least one side does not have active hydrogen among B and B', although the same, the oxy-alkylene chain which may be different from each other, or an alkyl group is expressed. In addition, when Above B and B' are oxy-alkylene chains, it is the oxy-alkylene chain of carbon numbers 1-6 preferably [it is desirable and] to the oxy-alkylene chain of carbon numbers 1-12, and a pan. Moreover, when B and B' is an alkyl group, it is the alkyl group of carbon numbers 1-6 preferably [it is desirable and] to the alkyl group of carbon numbers 1-12, and a pan. The silicone system compound which has the skeleton shown especially by the lower formula (4) made the current characteristic improve, and found out that it was effective for high-energy-izing of a cell.

[Formula 4]



Since a silicone skeleton generally has a ready bubble operation, although a silicon compound is used as a defoaming agent, in this invention, by making an alkoxy group add to a silicon compound, nonaqueous electrolyte and compatibility are made to improve and it thinks because the surface energy of the electrode interface of a non-water battery fell as this result. Although the compound of a front formula (4) is obtained by adding $CH_2=CH-CH_2-OH$ by the platinum catalyst, considering as the compound of a lower formula (6), and replacing the active hydrogen of this compound by the compound of a lower formula (5) with an oxy-alkylene chain further, as a compound of a front formula (4), active hydrogen is measured by IR and that in which active hydrogen does not exist is suitable.

[Formula 5]



In addition, in a front formula (4), (5), and (6), 0-10, and m, r and k of n are 1-10. a front formula (1) or the compound of (3) -- a solid electrolyte or the electrolytic-solution 100 weight section -- receiving -- 0.1 - 30 weight section -- desirable -- 0.1 - 10 weight *****

[0005] Next, although the composition of the non-water secondary lithium cell of this invention is described concretely, fundamentally, it is constituted by a positive electrode, a negative electrode, and the electrolyte. What dissolved the electrolyte salt in the non-aqueous solvent as the electrolytic solution is mentioned. as a non-aqueous solvent -- a carbonate solvent (propylene carbonate and ethylene carbonate --) Butylene carbonate, dimethyl carbonate, diethyl carbonate, an amide solvent (N-methyl formamide, N-ethyl formamide, and N,N-dimethylformamide --) N-methyl acetamide, N-ethyl acetamide, N-methyl PIROJIRINON, a lactone solvent (gamma-butyl lactone, gamma-valerolactone, and delta-valerolactone --) alcoholic solvents (ethylene glycol --), such as the 3-methyl-1 and 3-oxazolidine-2-ON A propylene glycol, a glycerol, a methyl cellosolve, 1, 2-butanediol, 1, 3-butanediol, 1, 4-butanediol, a diglycerol, Polyoxy alkylene glycol, a cyclohexane diol, a xylene glycol, etc., an ether solvent (a methylal, 1, 2-dimethoxyethane, 1, and 2-diethoxy ethane --) 1-ethoxy-2-methoxyethane, the alkoxy polyalkylene ether, etc., A nitril solvent (a benzonitrile, an acetonitrile, 3-methoxy propionitrile, etc.), phosphoric acid and a phosphoric-ester solvent (an orthophosphoric acid, a metaphosphoric acid, a pyrophosphoric acid, and a polyphosphoric acid --) 2-imidazolidinone solvents (1, 3-dimethyl-2-imidazolidinone, etc.), such as a phosphorous acid and trimethyl phosphate, A pyrrolidones solvent, a sulfolane solvent (a sulfolane, tetramethylen sulfolane), A furan solvent (a tetrahydrofuran, 2-methyl tetrahydrofuran, 2, 5-dimethoxy tetrahydrofuran), a dioxolane, a dioxane, and independent or two or more sorts of mixed solvents of a dichloroethane can be used. They are a carbonate solvent, an ether solvent, and a furan solvent preferably [among these]. Although there will be especially no limit if used as a usual electrolyte as an electrolyte salt in this invention For example, LiBR₄ (R is a phenyl group and an alkyl group), LiPF₆, LiSbF₆, LiAsF₆, LiBF₄, LiClO₄, CF₃SO₃Li, (CF₃SO₂)₃NLi, 3(CF₃SO₂) CLi, C₆F₉SO₃Li, and C₈F₁₇SO₃ -- Li, LiAlCl₄, etc. can be illustrated It is the electrolyte of sulfonic-acid system anions, such as CF₃SO₃Li, 3(CF₃SO₂) NLi, 3(CF₃SO₂) CLi, C₆F₉SO₃Li, and C₈F₁₇SO₃Li, preferably. Although the electrolytic solution is adjusted in the 0.5 mols/l. or more less than six mols [l.] range, it is within the limits of 3.5 mols/l. from 0.8 mols/l. preferably. As a solid polymer electrolyte, a polyethylene oxide, polypropylene oxide, A polyvinylidene fluoride, a polyacrylamide, etc. are made into a polymer matrix. The complex which dissolved the aforementioned electrolyte salt into the polymer matrix, or these gel bridge formation objects, The solid polymer electrolyte which graft-ized ionic dissociation machines, such as a low-molecular-weight polyethylene oxide and a crown ether, to the polymer principal chain, Or the solid polymer electrolyte which contains ionic dissociation machines, such as gel which added the solvent to these further, a low-molecular-weight polyethylene-oxide chain, and a crown ether, in a polymer skeleton, or the gel solid polymer electrolyte which made this contain the aforementioned electrolytic solution is mentioned.

[0006] The lithium alloy which consists of a lithium metal, aluminum, silicon, copper, zinc or tin, and a lithium as a negative electrode in this invention, the carbon material which are occlusion and the host compound which can be emitted irreversibly about a lithium ion, and ceramic material can be illustrated. The conductive carbon body or the insulating or half-conductive carbon body obtained as a carbon material by calcinating synthetic macromolecules, such as naturally-occurring polymers or a phenol system resin, a PAN system resin, a furan system resin, a polyamide system resin, and a polyimide system resin, can be illustrated. It is desirable to use graphite material as a main constituent as a carbon body of this invention. As a graphite material of this invention, the artificial graphite which used pitch coke besides a natural graphite, a needle coke, a fluid coke, gill box sonar corks, etc. as the raw material can be illustrated. As a positive active material of the non-water secondary lithium cell of this invention MnO₂, Mn₂O₃, CoO₂, NiO₂ and TiO₂, V₂O₅, V₃O₈, Cr₂O₃, Fe₂(SO₄)₃, Fe₂(MoO₄)₃, the metallic oxide of Fe₂(WO₄)₃ grade, Metallic sulfide, such as TiS₂, MoS₂, and FeS, these compounds, and the multiple oxide of a lithium, One sort or complex beyond it chosen from conductive polymers, such as a polyacetylene, the poly aniline, polypyrrole, the poly thiophene, the poly alkyl thiophene, the poly carbazole, the poly azulene, and a poly diphenyl benzidine, and a carbon body can be illustrated. As an electrolyte, the electrolytic solution mentioned above and a solid electrolyte are used. Moreover, separator can be used as occasion demands. The nonwoven fabric or textile fabrics which is low resistance, and the thing excellent in solution retentivity is used, for example, is chosen from one or more sorts of quality of the materials, such as

glass, polyester, Teflon, and polypropylene, to the ionic migration of an electrolytic solution as separator is mentioned. Although especially the gestalt of the cell of this invention is not limited, it can mount in the cell of various gestalten, such as coin, a sheet, a cylinder, and gum. An example explains this invention still more concretely below.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect] According to this invention, the highly efficient non-water lithium secondary battery which is excellent in a cycle property and can be charged also with high current density was offered.

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EXAMPLE

[Example]

The example 1 poly aniline 30 weight section was dissolved in the N-methyl-2-pyrrolidone of the 170 weight sections, and the vanadium-pentoxide 70 weight section was further distributed by the sand mill. Application dryness was carried out by the blade coating machine, and this paint solution was made into the positive electrode of 60 micrometers of one side at both sides of 25-micrometer etched aluminum foil. The negative-electrode active material layer was created so that the natural-graphite 80 weight section of 99.9% of purity and the tetrapod fluoroboric-acid lithium 10 weight section might be distributed in the 10wt% N-methyl-2-pyrrolidone solution 100 weight section of a polyvinyl-pyridine system resin (extensive glory chemistry), it might consider as a negative-electrode paint solution and the thickness of one side might be set to 80 micrometers at both sides of an SUS foil (thickness of 20 micrometers) (drying temperature of 100 degrees C). Through 25-micrometer separator [Celgard 3501 and a tradename (die cell company make)], the laminating of a positive electrode and the negative electrode was carried out, they were wound, and it considered as the cell of AA size. In the aforementioned (3) formula, to the aforementioned solution, m added to the ethylene carbonate / dimethoxyethane (1:1) solvent which contained two mol /of 2NLi(s) 1. as the electrolytic solution (CF₃SO₂) 3% of the weight, and used for it the silicone system compound which the both ends of 1, and r and k3 are n, and is a methyl group. Comparison performed the thing except the silicone system compound as an example 1 of comparison. The cell property of the cell of this example and the example 1 of comparison was shown in the following table 1.

[0008] It was presupposed that it is the same as that of an example 1 except having used the solid electrolyte solution shown below instead of the example 2 electrolytic solution. The photopolymerization nature solution which consists of the tetrapod fluoroboric-acid lithium 20 weight section, the propylene carbonate 51 weight section, 1, the 2-dimethoxyethane 16 weight section, the polyoxyethylene acrylate 12.8 weight section, the trimethylol-propane acrylate 0.2 weight section, and the benzoin-iso-propyl-ether 0.02 weight section was used as the solid-polymer-electrolyte solution. The amount addition of said of the silicone system compound used for this solid electrolyte solution in the example 1 was carried out. This adjustment liquid is heated and solidified after pouring in like the electrolytic solution. Comparison performed the thing except the silicone system compound as an example 2 of comparison. The cell property of this example and the example 2 of comparison was shown in the following table 1.

[Table 1]

example 1 66% 58% 1CmA 1 hour charge 86% 80% 74% 69% Energy : It is charge and discharge at 1/2CmA. Example 2 Example 1 of comparison Example of comparison 2 energy 485mAh 465mAh 388mAh 370mAh cycle property 500 times 500 times 350 times 400 times CmA [2] electric discharge 88% 81% The spark-discharge-energy cycle property after repeating 10 times: The number of times of a cycle until energy becomes 70% by the charge and discharge of 1/2CmA. 2CmA electric discharge, 1CmA 1 hour charge: Incidence-rate 2CmA electric discharge: 2CmA constant-current 2.5V cut-off electric discharge 1CmA 1 hour charge: 1CmA constant-current 3.7V low-battery charge 1 hour to the above-mentioned energy.

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CORRECTION or AMENDMENT

[Official Gazette Type] Printing of amendment by the convention of 2 of Article 17 of patent law.

[Section partition] The 1st partition of the 7th section.

[Date of issue] December 14, Heisei 11 (1999).

[Publication No.] Publication number 8-78053.

[Date of Publication] March 22, Heisei 8 (1996).

[**** format] Open patent official report 8-781.

[Filing Number] Japanese Patent Application No. 7-194161.

[International Patent Classification (6th Edition)]

H01M 10/40
10/36

[FI]

H01M 10/40 A
10/36 A

[Procedure revision]

[Filing Date] March 26, Heisei 11.

[Procedure amendment 1]

[Document to be Amended] Specification.

[Item(s) to be Amended] Claim 1.

[Method of Amendment] Change.

[Proposed Amendment]

[Claim 1] The lithium cell characterized by containing a silicone system compound in the electrolytic solution or a solid electrolyte in the non-water rechargeable battery which has the negative electrode and electrolyte containing at least one sort of active materials chosen from the group which consists of a host compound which forms a positive electrode and a lithium metal, a lithium alloy, a lithium, an intercalation compound, or a complex.

[Procedure amendment 2]

[Document to be Amended] Specification.

[Item(s) to be Amended] 0001.

[Method of Amendment] Change.

[Proposed Amendment]

[0001]

[Field of the Invention] this invention relates to the non-water secondary lithium cell which has the negative electrode which makes an active material the host compound which forms a lithium metal, a lithium alloy or a lithium ion, an intercalation compound, or a complex.

[Procedure amendment 3]

[Document to be Amended] Specification.

[Item(s) to be Amended] 0004.

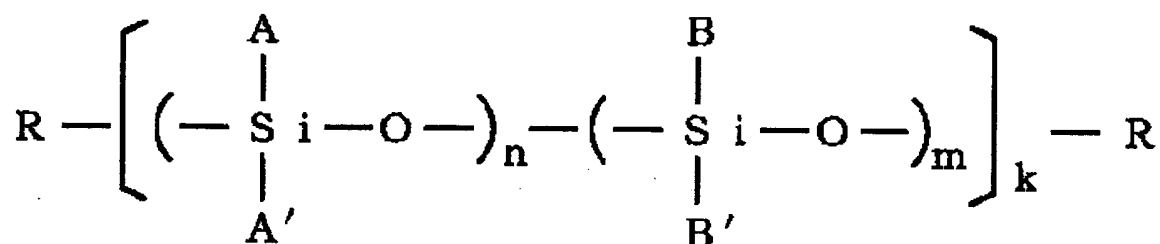
[Method of Amendment] Change.

[Proposed Amendment]

[0004]

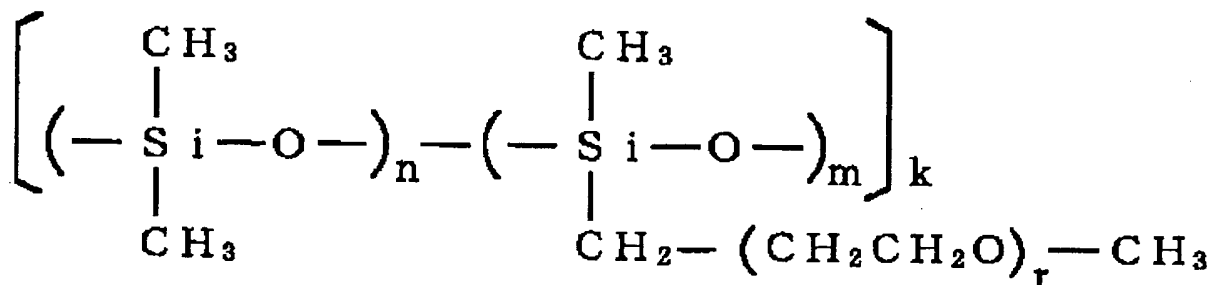
[Elements of the Invention] This invention persons found out that the purpose was reached in the non-water secondary lithium cell which has the negative electrode which makes an active material the host compound which forms a lithium metal, a lithium alloy or a lithium ion, an intercalation compound, or a complex by making a silicone system compound contain in the electrolytic solution or a solid electrolyte, as a result of examining the aforementioned technical problem wholeheartedly. As the aforementioned silicone system compound, the compound shown by the front formula (1) is mentioned. The remarkable effect was seen in the silicone system compound with which an oxy-alkylene adds to the side chain of an Si-O skeleton, and existence of active hydrogen is not checked especially. If the compound shown by the front formula (1) is shown more concretely, the silicone system compound shown by the following formula (3) will be mentioned.

[Formula 3]



in a front formula, R is an end group and this end group is the same -- or -- being different from each other -- desirable -- an alkyl group -- it is a methyl group still more preferably A and A' is the same or the alkyl group of carbon numbers 1-30 which may be different from each other, and is the alkyl group of carbon numbers 1-6 preferably [it is desirable and] to the alkyl group of carbon numbers 1-12, and a pan. B and B' is an oxy-alkylene chain which does not have active hydrogen and with which at least one side does not have active hydrogen among B and B', although the same, the oxy-alkylene chain which may be different from each other, or an alkyl group is expressed. In addition, when Above B and B' are oxy-alkylene chains, it is the oxy-alkylene chain of carbon numbers 1-6 preferably [it is desirable and] to the oxy-alkylene chain of carbon numbers 1-12, and a pan. Moreover, when B and B' is an alkyl group, it is the alkyl group of carbon numbers 1-6 preferably [it is desirable and] to the alkyl group of carbon numbers 1-12, and a pan. The silicone system compound which has the skeleton shown especially by the lower formula (4) made the current characteristic improve, and found out that it was effective for high-energy-izing of a cell.

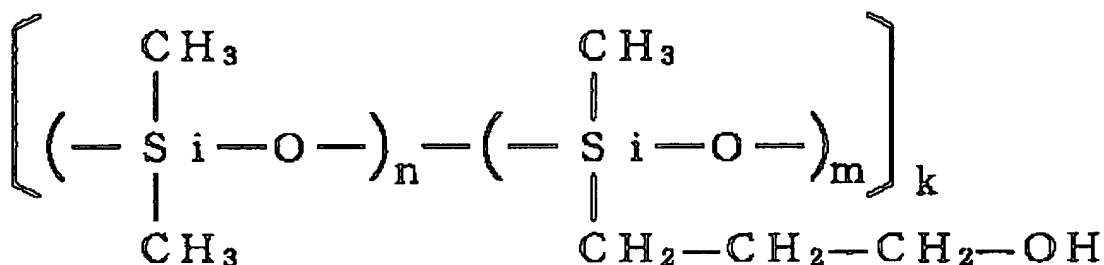
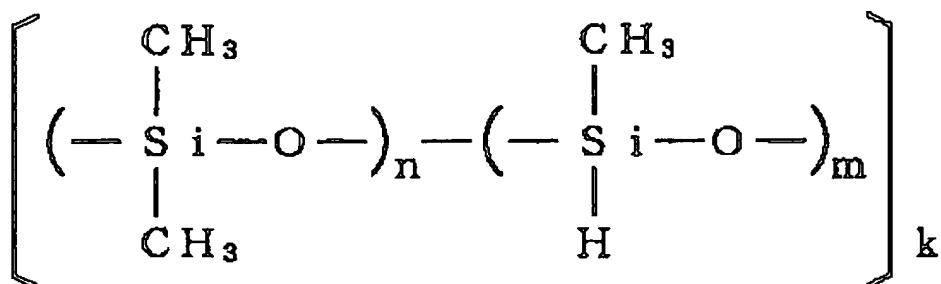
[Formula 4]



Since a silicone skeleton generally has a ready bubble operation, although a silicon compound is used as a defoaming agent, in this invention, by making an alkoxy group add to a silicon compound, nonaqueous electrolyte and compatibility are made to improve and it thinks because the surface energy of the electrode interface of a non-water battery fell as this result. Although the compound of a front formula (4) is obtained by adding $CH_2=CH-CH_2-OH$ by the platinum catalyst, considering as the compound of a lower formula (6), and replacing the active hydrogen of this compound by the compound of a lower formula (5) with an oxy-alkylene chain further, as a compound of a front

formula (4), active hydrogen is measured by IR and that in which active hydrogen does not exist is suitable.

[Formula 5]



In addition, in a front formula (4), (5), and (6), 0-10, and m, r and k of n are 1-10. a front formula (1) or the compound of (3) -- a solid electrolyte or the electrolytic-solution 100 <TXF FR=0006 HE=010 WI=080 LX=1100 LY=1600> weight section -- receiving -- 0.1 - 30 weight section -- desirable -- 0.1 - 10 weight *****

[Translation done.]

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